SYNTHESIS, CHARACTERIZATION AND APPLICATION OF HOLLOW TITANIA MICROSPHERES CONTAINING SILVER AND GOLD NANOPARTICLES IN THE PHOTODEGRADATION OF PESTICIDES

AFROUZ BAHARVAND

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Universiti Teknologi Malaysia

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To my beloved Father and Mother

Uncle

Brothers and Sisters

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In the name of Allah, the Most Beneficent, the Most Merciful Alhamdulillah, thanks to Allah with his blessings, bounties and consents I could finally complete my studies.

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ABSTRACT

Hollow titania (TiO_2) materials have unique properties, such as multiple light reflection and diffraction, surface permeability, light-harvesting capability and their technological importance in the fields of medicine, pharmacy, materials science, water treatment, catalyst and photocatalyst. The research described in this dissertation is a comprehensive account of an attempt to correlate structural and physicochemical properties of hollow TiO_2 microspheres containing silver (Ag) and gold (Au) nanoparticles with their photocatalytic properties. It is hypothesized that hollow TiO_2 microspheres containing Ag and Au nanoparticles can enhance light harvesting and also facilitates the charge separation, in the photodegradation of pesticides. The location of Ag and Au, whether inside or outside the hollow titania, may also affect the photocatalytic activity. The synthesis of hollow TiO_2 microspheres containing Ag or Au nanoparticles was conducted by using fructose as the precursor *via* hydrothermal method. The fructose-derived carbonaceous spheres obtained were then used as the template for the synthesis of hollow crystalline TiO_2 microspheres photocatalysts. These photocatalysts were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, diffuse reflectance ultraviolet–visible (DR UV–Vis) spectroscopy, photoluminescence (PL) spectroscopy, thermogravimetry (TG) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption and chemical analysis by X-ray fluoresence (XRF) spectroscopy. TiO_2 photocatalyst obtained was in the crystalline anatase phase and spherical in shape, with cavity inside the spheres. The existence of Ag and Au was confirmed by XRD, XRF, EDX, TEM and HRTEM. DR UV–Vis spectra revealed that the hollow TiO_2 containing noble metals have absorption spectrum in a longer wavelength in comparison to that of commercial TiO_2. By employing pesticides, namely paraquat dichloride, diazinon, imazalil sulfate, atrazine, lindane and chlorpyrifos, as the target compounds, the photocatalytic activity investigation of the hollow TiO_2 microspheres was carried out. The photodegradation of pesticides over hollow TiO_2 microspheres containing Ag or Au nanoparticles was correlated with the type of pesticides in the following decreasing order: chlorpyrifos > diazinon > γ-lindane > imazalil sulphate > paraquat dichloride > atrazine. It was also observed that the location of Ag or Au, whether inside or outside the microspheres, is an important factor to achieve high photocatalytic activity for the decomposition of pesticides. The photocatalytic activity results revealed that the attachment of Ag nanoparticles outside the TiO_2 microspheres was the most effective location in the photodegradation of these pesticides, with 84% degraded. Based on the above results, it is suggested that the location of the Ag or Au as electron scavengers on the hollow TiO_2 microspheres plays an important role in the photocatalytic activities of these materials.

ABSTRAK

Bahan berongga titania (TiO_2) mempunyai sifat-sifat unik seperti pemantulan dan pembelauan cahaya yang berbilang, kebolehtelapan permukaan, kemampuan memerangkap cahaya dan kepentingan teknologi dalam bidang perubatan, farmasi, sains bahan, perawatan air, mangkin dan fotomangkin. Penyelidikan yang dinyatakan dalam disertasi ini adalah penerangan komprehensif mengenai percubaan untuk menghubungkaitkan sifat-sifat struktur dan fizikokimia mikrosfera TiO_2 berongga yang mengandungi nanopartikel perak (Ag) dan emas (Au) dengan ciri-ciri pemfotomangkinan. Hipotesis menyatakan bahawa mikrosfera TiO_2 berongga yang mengandungi nanopartikel Ag dan Au boleh meningkatkan pemerangkapan cahaya dan juga memudahkan pemisahan cas dalam fotodegradasi racun perosak. Lokasi nanopartikel Ag dan Au, sama ada di dalam atau di luar titania berongga juga boleh menjejaskan aktiviti pemfotomangkinan. Sintesis mikrosfera TiO_2 berongga yang mengandungi nanopartikel Ag dan Au telah dilakukan menggunakan fruktosa sebagai bahan pemula melalui kaedah hidroterma. Sfera berkarbon terbitan fruktosa yang diperoleh kemudiannya digunakan sebagai templat untuk sintesis fotomangkin mikrosfera TiO_2 hablur berongga. Fotomangkin ini dicirikan dengan menggunakan pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi ultralembayung-nampak pantulan baur (DR UV–Vis), spektroskopi pendarcahaya (PL), analisis termogravimetri (TG), mikroskopi elektron pengimbasan (SEM), mikroskopi elektron penghantaran (TEM), penjerapan nitrogen dan analisis kimia menggunakan spektroskopi pendarfluor sinar-X (XRF). Fotomangkin TiO_2 yang terhasil adalah dalam fasa anatas berhablur dan berbentuk sfera, dengan kewujudan rongga dalam sfera tersebut. Kewujudan Ag dan Au telah disahkan menggunakan XRD, XRF, EDX, TEM dan HRTEM. Spektrum DR-UV-Vis mendedahkan bahawa TiO_2 berongga yang mengandungi logam adi mempunyai spektrum penyerapan pada panjang gelombang yang lebih panjang berbanding TiO_2 komersial. Dengan menggunakan racun perosak, iaitu parakuat diklorida, diazinon, imazalil sulfat, atrazin, lindane dan klorpirifos sebagai sebatian sasaran, kajian aktiviti pemfotomangkinan mikrosfera TiO_2 berongga telah dijalankan. Fotodegradasi racun perosak oleh mikrosfera TiO_2 berongga yang mengandungi nanopartikel Ag atau Au terhadap jenis racun perosak telah dikorelasikan dengan jenis racun perosak dalam urutan yang menurun sebagai berikut: klorpirifos > diazinon > γ-lindane > imazalil sulfat > parakuat diklorida > atrazin. Turut diperhatikan juga bahawa kedudukan Ag atau Au, sama ada di dalam atau di luar mikrosfera, adalah faktor penting untuk mencapai aktiviti pemfotomangkinan yang tinggi bagi fotodegradasi racun perosak. Keputusan aktiviti pemfotomangkinan mendedahkan bahawa penempatan nanopartikel Ag di luar mikrosfera TiO_2 merupakan lokasi paling berkesan bagi fotodegradasi racun perosak, dengan sebanyak 84% terdegradasi. Berdasarkan keputusan di atas, adalah dicadangkan bahawa lokasi Ag atau Au sebagai pengaut elektron pada mikrosfera TiO_2 berongga memainkan peranan penting dalam aktiviti pemfotomangkinan bahan ini.

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LIST OF ABBREVIATIONS / SYMBOLS

A	-	Absorbance
Ag	-	Silver
$AgNO_3$	-	Silver nitrate
Al_2O_3	-	Aluminum oxide
AOP	-	Advanced oxidation process
atm	-	Atmosphere
Au	-	Gold
a.u.	-	Arbitrary unit
b	-	Path length of the sample
$BaSO_4$	-	Barium sulphate
BET	-	Brunauer Emmet Teller
BHC	-	Benzene hexachloride
c	-	Concentration
C	-	Carbon
C_0	-	Concentration of the solution before irradiation
CB	-	Conduction band
CeO_2	-	Cerium(IV) oxide
CH_4	-	Methane
CO_2	-	Carbon dioxide
CO	-	Carbon monoxide
Co	-	Cobalt
$(CO(NH_2)_2$	-	Urea
CoO	-	Cobalt(II) oxide
Co_3O_4	-	Cobalt(II,III) oxide
Cr_2O_3	-	Chromium(III) oxide
CS	-	Carbon sphere

CTAB	-	Cetyltrimethylammonium bromide
C_t	-	Concentration of the solution after time t
CVD	-	Chemical Vapour Deposition
Cu	-	Copper
Cu k_α	-	X-ray diffraction from copper kα energy levels
Cu_2O	-	Copper(I) oxide
DMF	-	N,N-Dimethylmethanamide (Dimethylformamide)
DP	-	Deposition-precipitation
DTG	-	Differential Thermal Gravimetric
DR UV–Vis	-	Diffuse reflectance Ultraviolet–Visible
ECD	-	Electron capture detector
EtOH	-	Ethanol
e^-	-	Electron
e^-_{CB}	-	Electron in conduction band
EDX	-	Energy Dispersive X-Ray Spectroscopy
EG	-	Ethylene glycol
e.g.	-	For example
E_g	-	Band gap energy
E_F	-	Fermi energy
EM	-	Electromagnetic
EPA	-	Environmental Protection Agency
et al.	-	And others (Latin: *et alia*)
etc.	-	And the others (Latin: *et cetera*)
α-Fe_2O_3	-	Iron(III) oxide (Hematite)
FESEM	-	Field Emission Scanning Electron Microscopy
FESEM-EDX	-	Field Emission Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy
FTIR	-	Fourier Transform Infrared
FWHM	-	Full width at half maximum
Ga_2O_3	-	Gallium(III) oxide
GaN	-	Gallium nitride
GC	-	Gas Chromatography
GC-μECD	-	Gas Chromatography Microelectron Capture Detector

h^+	-	Holes
h^+_{VB}	-	Positive hole in valence bond
H_2	-	Hydrogen
$HAuCl_4.3H_2O$	-	Chloroauric acid trihydrate
α-HCH	-	α-hexachlorocyclohexane
β-HCH	-	β-hexachlorocyclohexane
HCl	-	Hydrochloric acid
HDP	-	Homogeneous deposition–precipitation
He	-	Helium
HMF	-	5-hydroxymethyl-2-furaldehyde
H_2O	-	Dihydrogen monoxide
H_2O_2	-	Hydrogen peroxide
HOMO	-	Highest occupied molecular orbital
$h\nu$	-	Energy (photon)
HRTEM	-	High Resolution Transmission Electron Microscopy
ID	-	Identification
i.e.	-	That is (Latin: *id est*)
IE	-	Ionization energy
ICDD	-	International Centre for Diffraction Data
In_2O_3	-	Indium(III) oxide
IUPAC	-	International Union of Pure and Applied Chemistry
KBr	-	Potassium bromide
K–M	-	Kubelka-Munk
K_{OW}	-	Octanol–water distribution coefficient
La_2O_3	-	Lanthanum(III) oxide
LD_{50}	-	Median lethal dose
LUMO	-	Lowest unoccupied molecular orbital
LSPR	-	Localized surface plasmon resonance
Lu_2O_3	-	Lutetium(III) oxide
MB	-	Methylene blue
MgO	-	Magnesium oxide
Mn_3O_4	-	Manganese(II,III) oxide
MO	-	Methyl orange

N_2	-	Molecular nitrogen
NaOH	-	Sodium hydroxide
NH_4OH	-	Ammonium hydroxide
NiO	-	Nickel(II) oxide
O_2	-	Oxygen
OCPs	-	Organochlorine Pesticides
OPPs	-	Organophosphorus Pesticides
O_2^-	-	Peroxo
O^{2-}	-	Oxide ion
OH	-	Hydroxyl
•OH	-	Hydroxyl radical
OH^-	-	Hydroxyl ion
P25	-	Comercial titanium dioxide
Pd	-	Palladium
pH	-	Acidity or basicity measurement
PL	-	Photoluminescence
i-PrOH	-	2-Propanol
PSA	-	Poly(styrene-methyl acrylic acid)
Pt	-	Platinum
PVP	-	Polyvinylpyrrolidone
R	-	Reflectance
R^2	-	Linear least square
SAED	-	Selected area electron diffraction
Sb	-	Antimony
SEM	-	Scanning Electron Microscopy
SEEM	-	Sanderson electronegativity equivalence method
S_{int}	-	Sanderson intermediate electronegativity
SiO_2	-	Silica
Sn	-	Tin
SnO_2	-	Tin(IV) oxide
SPR	-	Surface plasmon resonance
T	-	Transmittance
T	-	Temperature

t	-	Time
TBOT	-	Titanium(IV) buthoxide
TBT	-	Tetrabutyl titanate
TEM	-	Transmission Electron Microscopy
TEOS	-	Tetraethyl orthosilicate
TEOT	-	Titanium(IV) ethoxide
Ti	-	Titanium
Ti^{4+}	-	Titanium ion
$TiCl_4$	-	Titanium tetrachloride
TiF_4	-	Titanium tetrafluoride
TiO_2	-	Titanium dioxide
TGA	-	Thermal Gravimetric Analysis
TG–DTG	-	Thermal Gravimetric and Differential Thermal Gravimetric
TTEAIP	-	Titanium-(triethanolaminato) isopropoxide
TTIP	-	Titanium(IV) isopropoxide
UV	-	Ultraviolet
UV–Vis	-	Ultraviolet–Visible
V	-	Volume
v	-	Wavenumber
VB	-	Valence band
via	-	By way of (Latin: viā)
vs	-	Versus
WO_3	-	Tungsten trioxide
wt %	-	Weight percentage
XRD	-	X-Ray Diffraction
XRF	-	X-ray Fluorescence Spectroscopy
Z	-	Atomic number
ZnO	-	Zinc oxide
ZnS	-	Zinc sulphide
ZrO_2	-	Zirconium(IV) oxide
A	-	Absorbance
α	-	Absorption coefficient
D	-	Crystal size

h	-	Planck constant
λ	-	Wavelength
θ	-	Theta (Bragg angle)
~	-	Approximately
γ	-	Gamma
η	-	Percent degradation
R_{∞}	-	Diffuse reflectance
s	-	Scattering factor
ε	-	Molar absorptivity

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CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Hollow sphere is a branch of shell-structured materials which consists of solid organic or inorganic shells with enclosed gas-filled cavity. It is believed that the inner “nano or micro space” of the mentioned structures, when coupled with chemical functionality of the boundary materials, could improve both scientific attraction and aesthetic beauty. Increasing research works are being reported on the modification of hollow materials after the introduction of hollow spheres fabrication (Abdelaal, 2013; Xiao *et al.*, 2008). In the last decade, these hollow interior materials were compared to other solid spheres. The hollow interior materials were found to have greater potentials due to their peculiar and better physicochemical properties, such as large surface area, low density, surface permeability and stability (Ren *et al.*, 2005). As such, they have wider range of technological and scientific applications (Ren *et al.*, 2005). Furthermore, the spherical form has lower surface to volume ratio, and therefore, has higher adsorption capacity.

These hollow materials represent a myriad of application in the areas of material science, paint industries, pharmaceutical industries, in water treatment and medicinal field (Caruso, 2000; Sun *et al.*, 2006; Yuan *et al.*, 2003; Yu and Zhang, 2010; Caruso *et al.*, 2001a). Other applications are found in the protection of sensitive compounds (such as enzymes and proteins), chromatography and catalysis (Caruso, 2000; Li *et al.*, 2007b; Sun *et al.*, 2006; Lüdtke *et al.*, 1997; Yuan *et al.*, 2003; Yu and Zhang, 2010; Caruso *et al.*, 2001a). Hollow inorganic shells that are meso or macroporous in nature could also be used for the encapsulation of chemicals, such as in the controlled-release of drugs, cosmetics, dyes and inks, coating, as inorganic fillers, artificial cells and composites (Caruso, 2000; Li *et al.*, 2007b; Sun *et al.*, 2006; Yuan *et al.*, 2003; Caruso *et al.*, 2001a). Hollow oxide materials could also be modified to be highly porous, which could be used as adsorbents. Other application of such materials could be exploited based on the morphology, chemical composition and the size of the materials (Yu *et al.*, 2007b; Yuan *et al.*, 2003; Zhu *et al.*, 2006; Zhu *et al.*, 2005).

Various physical and chemical methods, such as sol–gel, emulsion/interfacial polymerization, spray-drying, colloidal templating, surfactant assisted solvothermal decomposition and template free approaches have been employed to produce nano and micro hollow material (Nakashima and Kimizuka, 2003; Peng *et al.*, 2003; Yang and Zeng, 2004a; Yu *et al.*, 2006; Caruso *et al.*, 2001a). Out of all these methods, sacrificial templating approach is the most widely and efficient technique used in producing micro and nano particles with hollow structured that are based on the synthesis of core–shell composites (Velikov and van Blaaderen, 2001; Wang *et al.*, 2004; Wang *et al.*, 2002). The core could then be removed either by heating (calcination) or dissolution in a solvent (Caruso *et al.*, 2001a).

Generally, manipulation of hollow material can be achieved by template directed synthesis technique. It is believed that the shape and size of the hollow materials are exclusively determined by the dimensions and shapes of the template (Sun and Li, 2004b; Lou *et al.*, 2008a). There are two main types of templates, *i.e.* (i) hard and (ii) soft templates. These templates are often employed in producing hollow spheres that have homogeneous and dense layers. For hard template assisted synthesis, inorganic and organic solid materials such as silica spheres (Salgueirino-Maceira *et al.*, 2005), carbon (Caruso *et al.*, 2001b) and polymer (Shiho and Kawahashi, 2000) are normally employed as the colloidal templates. The wider applications of these templates could be ascribable to their availability in relatively large amounts, narrow size distribution, and easy synthetic procedures by employing well-known formulations (Lou *et al.*, 2008a). These templates could be removed either by dissolution in selected solvent or by calcination at higher temperature in air to obtain the hollow structures. Other colloidal systems, e.g. carbon nanosphere and nanoparticle of metals and metal oxides, were also used as templates to prepare hollow structures (Yu and Wang, 2008; Lou *et al.*, 2008a). Carbon sphere templates could be effectively used to prepare metallic and metallic oxide hollow spheres (Yu and Wang, 2008; Lou *et al.*, 2008a; Shin *et al.*, 2008). This is because carbon template is hydrophilic and functionalized with ─OH and ─C═O groups on its surface (Zheng *et al.*, 2006). This functionalization makes the surface modification of carbon spheres unnecessary. In soft template assisted synthesis, polymer micelles, liquid crystals, microemulsion droplets, surfactant vesicles and gas bubbles were mostly employed (Fowler *et al.*, 2001; Schmidt and Ostafin, 2002; Wu *et al.*, 2003). For the soft templates, the morphology of the hollow products is usually poor because of the deformability of the soft templates.

Another material which could be used to produce hollow spheres is titania (TiO_2). Its properties make it a good candidate with numerous applications, such as in catalyst supports, gas sensing, solar cells and wastewater treatments (Kumar *et al.*, 1993; Park *et al.*, 1999; Yu *et al.*, 2002b). The unique photocatalytic properties also make TiO_2 being widely employed for the oxidation of the organic pollutants in wastewater (Fabiyi and Skelton, 2000; Syoufian *et al.*, 2007).

Hollow TiO_2 microspheres are associated with high surface area, low density, easy recovery, ability to deliver of drugs, high surface permeability (Yu *et al.*, 2007b) and have multiple light reflection and diffraction (Kondo *et al.*, 2007). It is also believed that the structural features also improved its light harvesting ability by allowing more light to penetrate into its interior (Kondo *et al.*, 2007; Li *et al.*, 2007a). This light harvesting ability makes hollow TiO_2 as promising photocatalyst (Kondo *et al.*, 2007). The photocatalytic activity of TiO_2 is due to the formation of a photo-induced electron and a positive hole which occurs as a result of ultraviolet light absorption which corresponds to the energy gap (Herrmann, 1999). These species are believed to be mobile and are capable of initiating many photocatalytic reactions. However, the fast recombination of photogenerated electrons and holes limits both the photocatalytic efficiency and activity of TiO_2. Therefore, the photocatalytic activity of TiO_2 can be improved by controlling the steps involved during the photocatalysis by TiO_2. These steps include: e^- and h^+ generation, followed by their separation, migration and the reaction on the surface with adsorbed species. The photoinduced charge separation in bare TiO_2 particles has a very short life time, which is due to the recombination of charges. So, it is vital to prevent electron–hole recombination before a designated chemical reaction occurs on the surface of TiO_2. High recombination rate of the photogenerated electron–hole pairs limit the industrial application of TiO_2. Since charge separation is found to be a major problem, many attempts were made to improve the photocatalytic activity of TiO_2 by modifying the surface or bulk properties. This includes coupling of two semiconductors, metal deposition, surface chelation and doping (Xu *et al.*, 2005; Chatterjee and Mahata, 2002; Tada *et al.*, 1998).

High rate of photogenerated electron–hole pairs recombination process can be minimized by loading metal nanoparticles on the surface of TiO_2 (Subramanian *et al.*, 2004). In this system, photopromoted electrons are captured by noble metal nanoparticles, which have Fermi level energy lower than the conduction band potential of the semiconductor with a consequent increase of the overall photocatalytic efficiency, especially under UV light (Subramanian *et al.*, 2004). Although, this type of catalyst's structure is effective, metals on the surface of the semiconductor are easily corroded and dissolved (Hirakawa and Kamat, 2005). To overcome these drawbacks, the noble metals are incorporated as the core and the semiconductor, such as TiO_2, acts as the shell (TiO_2@noble metal rattles).

The TiO_2@noble metal rattles are regarded as double-functionalized catalysts. This catalyst could also be employed in catalytic reduction because of the noble metal inside, as well as in the photocatalytic reactions due to the synergistic interactions between noble metal nanoparticles and TiO_2 shells. Recently, for silver core and TiO_2 shell (TiO_2/silver) nanoparticles, the photoinduced electrons in TiO_2 shell were injected into the silver core using illuminated ultraviolet light (Hirakawa and Kamat, 2005).

For this work, the attention is focused on the synthesis of hollow TiO_2 and noble metals (silver (Ag) and gold (Au)) modified hollow anatase TiO_2, which can enhance light harvesting and also facilitates the charge separation. First, hollow anatase TiO_2 was synthesized through a modified template route. Second, two types of noble metals modified hollow anatase TiO_2, such as gold core anatase TiO_2 shell (TiO_2@Au rattle), silver core anatase TiO_2 shell (TiO_2@Ag rattle) and surface modified hollow anatase TiO_2 with noble metals were prepared. Lastly, the photocatalytic activity was investigated using pesticides and the effect of metals modification in enhancing the photocatalytic efficiency was investigated. A schematic presentation of the research plan in achieving these goals is shown in Figure 1.1.

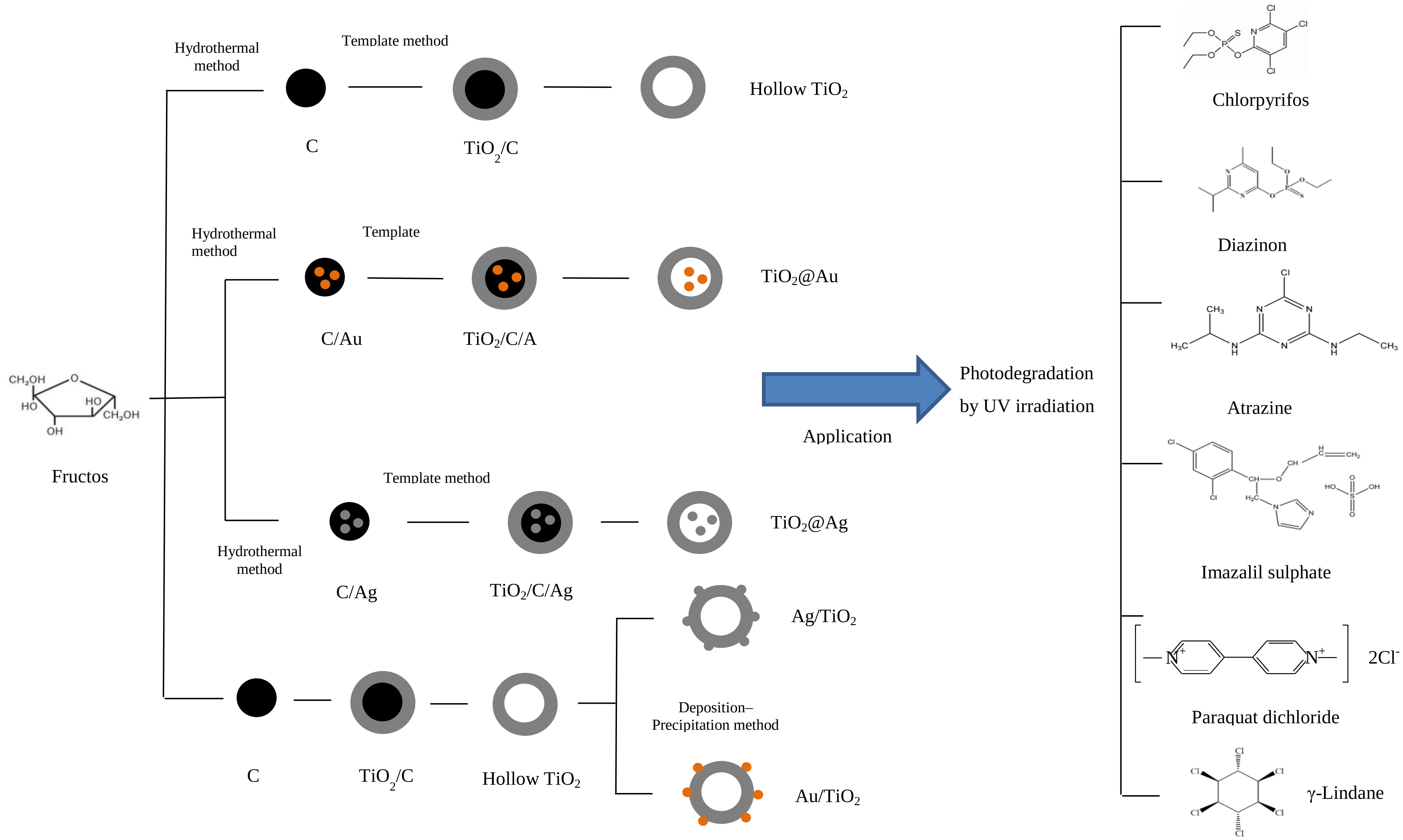

Figure 1.1: Schematic presentation of the research plan

1.2 Problem Statement

TiO_2, a semiconductor, has a wide range of applications due to its interesting properties. Due to its high refractivity, high thermal stability, high chemical stability and non toxic, TiO_2 has been used as pigment, functional filler, sensor material and catalyst (Yu and Zhang, 2010; Chen and Mao, 2007). However, several factors limit the photocatalytic activity of TiO_2. High light harvesting, slow electron-hole recombination rate and rapid electron transport are vital for good photocatalytic activity. Hollow spheres are believed to have higher light harvesting efficiency and rapid charge carriers motion (Yu and Zhang, 2010). These could be due to their hollow structures, closely arranged interpenetrating networks and large internal surface areas (Yu and Zhang, 2010).

In order to synthesize hollow TiO_2 with improved properties, many different approaches have been taken. In this research, we adopted the synthesis route described by Ao *et al*. (2008). They reported a hard templating method using glucose as the precursor. In this work, instead of glucose, fructose was used as the precursor in the synthesis of hollow TiO_2 spheres. Employing fructose could reduce the time and reaction temperature during the synthesis of template as compared to when glucose was used. The hollow TiO_2 spheres' particle size was smaller when glucose was employed as the template. It was also found that the recombination rate of electron–hole pairs was greatly reduced, which increased the photocatalytic efficiency of the synthesized hollow TiO_2 by the addition of electron scavengers, such as Ag and Au. In this context, noble metal modified hollow anatase TiO_2 photocatalysts *i.e.* Ag, Au outside/inside hollow anatase TiO_2 with the aim of improving the efficiency, have been designed. The effect of noble metal was investigated based on the photocatalytic efficiency of the catalysts on the photodecomposition of pesticides.

Based on the above problem, the research question can be defined as follow: Are the noble metals/hollow anatase TiO_2 as potential photocatalysts in pesticides degradation under UV light irradiation?

1.3 Research Objectives

- To synthesize and characterize hollow anatase TiO_2 spheres containing silver and gold nanoparticles.
- To evaluate the photocatalytic activity of the prepared noble metal–hollow anatase TiO_2 in the photodegradation of pesticides.
- To investigate the relationship between the structure and the photocatalytic activity of the photocatalysts in the decomposition of pesticides.

1.4 Significance of the Study

In this research, The driving forces for the synthesis of hollow anatase TiO_2 modified with noble metals and their use as the photocatalyst in the degradation of paraquat dichloride, imazalil sulphate, lindane, chlorpyrifos, diazinon and atrazine pesticides were the large light harvesting efficiency, multiple light diffraction and reflection, high photocatalytic activity (a special case of the application of nanosized noble metal-containing hollow TiO_2) and high stability. Apart from that, this synthesis approach only utilized template and the metal precursor to prepare hollow TiO_2 spheres without any chemical additives.

1.5 Scope of the Study

The scope of this work includes the synthesis of carbon spheres, hollow anatase TiO_2, modified hollow anatase TiO_2 with noble metals nanoparticles and the study of the structure-properties relationship of the samples in order to achieve high photocatalytic activity in photodegradation of pesticides. First, the effect of different synthesis parameters, which includes temperature, fructose concentration and duration, on the as-obtained template, which acts as the size and shape directing agent, were studied. Second, hollow anatase TiO_2 powders with different structures were successfully synthesized by different methods. The morphological, structural and thermal properties of the products were characterized by using Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), X-ray diffraction spectroscopy (XRD), field emission scanning electron microscopy (FESEM), Brunauer–Emmett–Teller surface area analysis, thermogravimetric and differential thermal gravimetric (TG–DTG), photoluminescence spectroscopy (PL) and diffuse reflectance ultraviolet visible spectroscopy (DR UV–Vis). The photodegradation of pesticides was used to study the samples' photocatalytic performance. The photodegradation was conducted in the presence of UV light and was analyzed using UV–Visible spectrophotometer and gas chromatograph (GC) equipped with a µECD system. All photodegradation processes were conducted at ambient temperature and pressure. The influence of several parameters, including the type of noble metals, location of the noble metals and chemical structure of pesticides, on the photocatalytic properties of the photocatalysts was then evaluated considering data obtained from GC–µECD and UV–Visible studies.

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